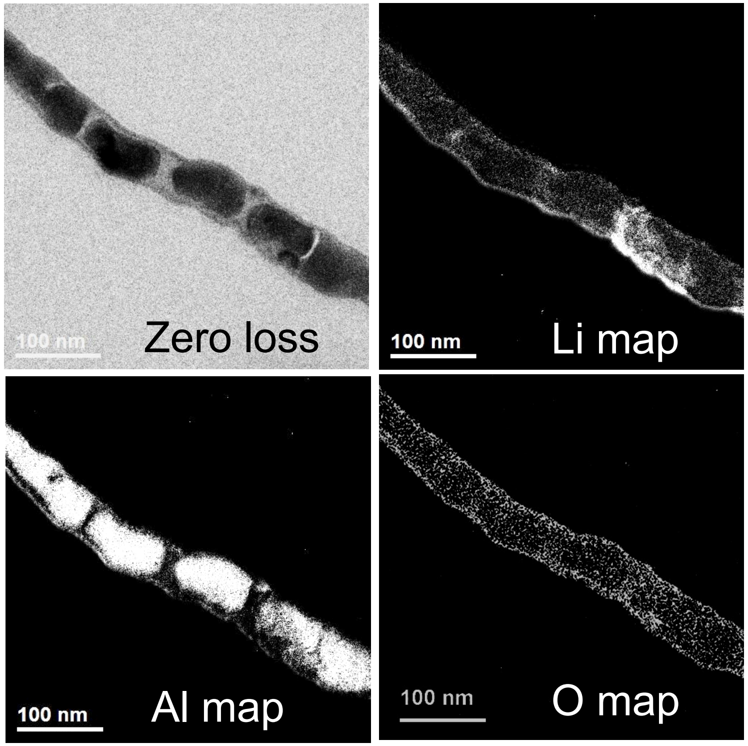
SAND2011-9126P

In situ TEM Observation of Pulverization of Aluminum Nanowires and Evolution of the Thin Surface Al_2O_3 Layers During Lithiation-Delithiation Cycles



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Sandia National Labs*, Albuquerque, NM

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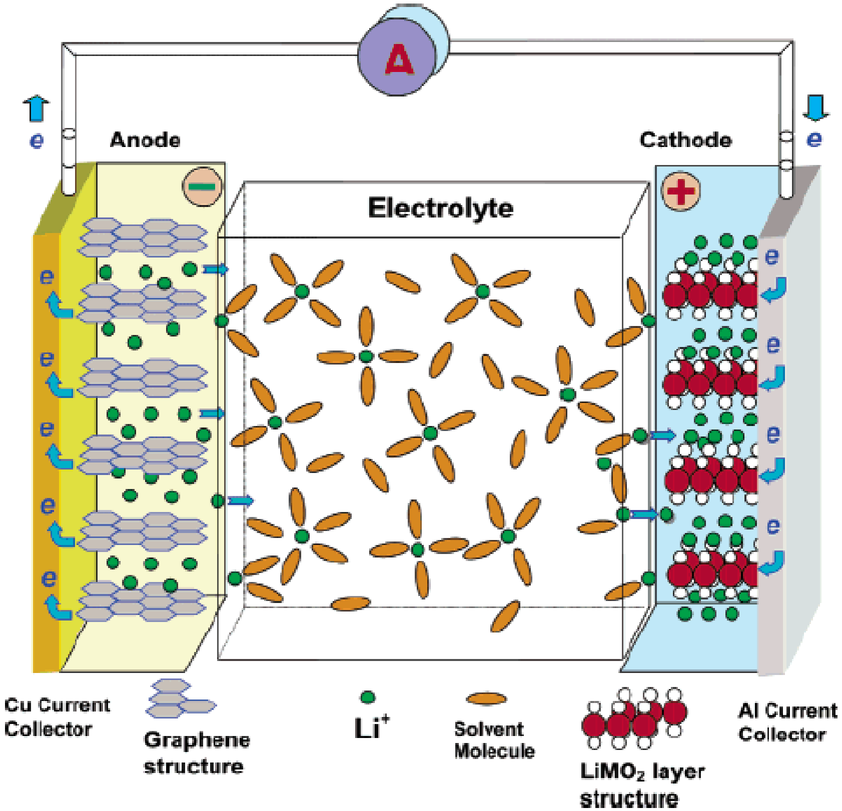
Outline

- Background
- Experimental setup of *in situ* TEM battery test
- Pulverization of Aluminum Nanowires
- Evolution of the Thin Surface Al_2O_3 Layers
- Conclusions

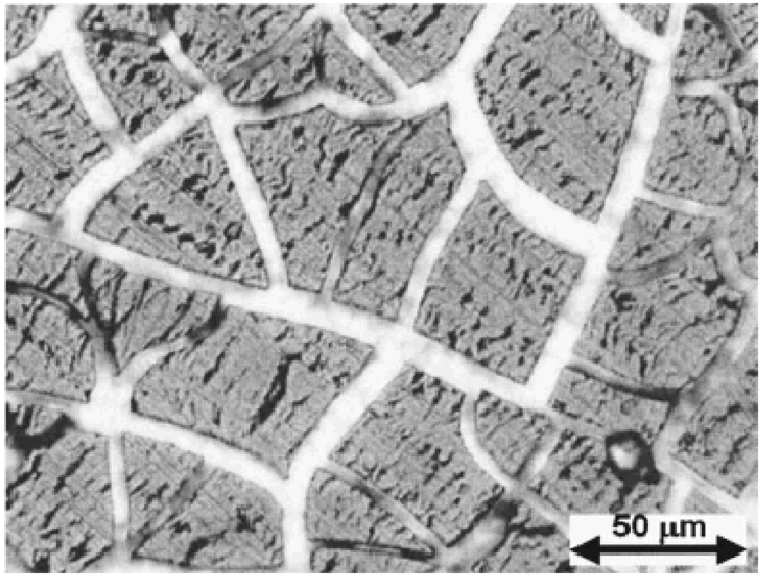
Motivation



High energy/power density
Good cyclability
Low cost

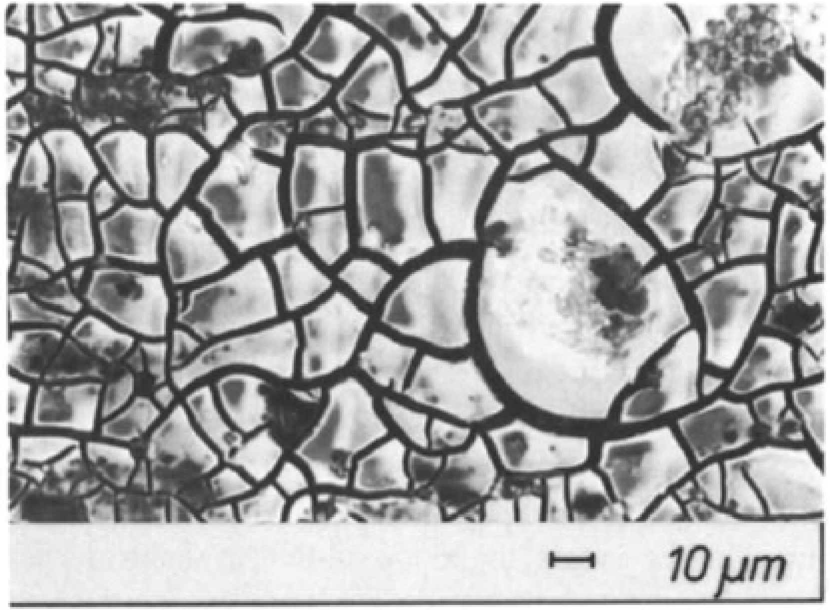
Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 2-4, 2007

Pulverization of the active materials



Optical micrograph of a Li-alloy film after expansion and contraction

Dahn et al., ***Electrochem. Solid-State Lett.*** 4, A137 (2001)

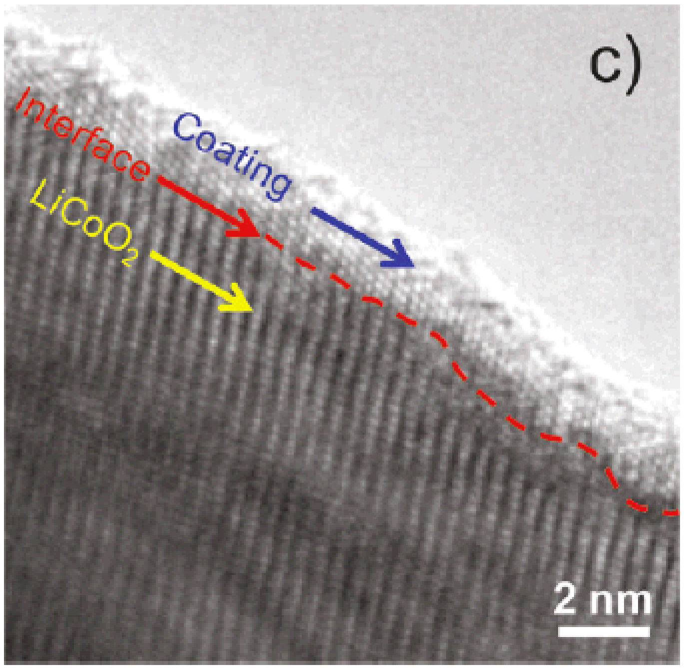


SEM image of a beta-LiAl film after 30 cycles

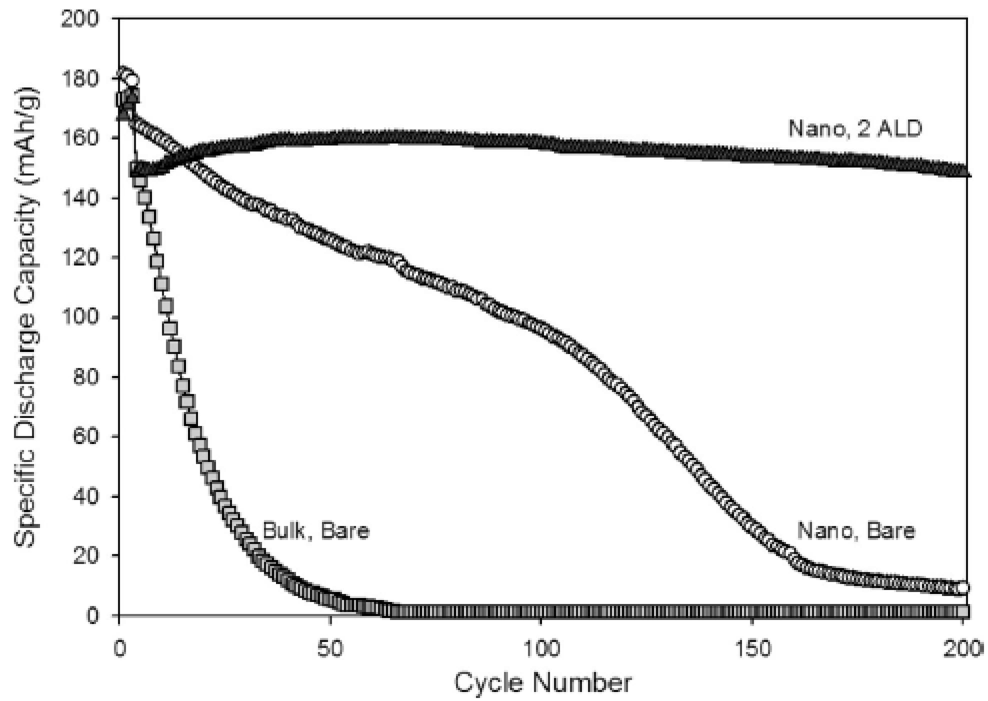
Besenhard et al., ***Solid State Ionics*** 40/41, 525 (1990)

Such pulverization processes, which involve the nucleation and evolution of voids or crack initiation, are not well understood.

The function of Al_2O_3 coating on active materials



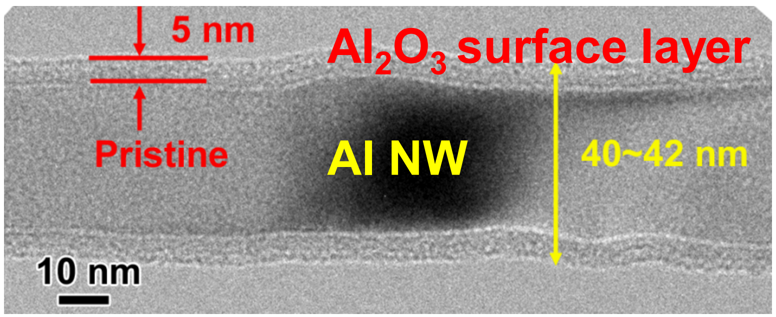
ALD Al_2O_3 coating on $LiCoO_2$



Scott et al., ***Nano Lett.*** 11, 414 (2011)

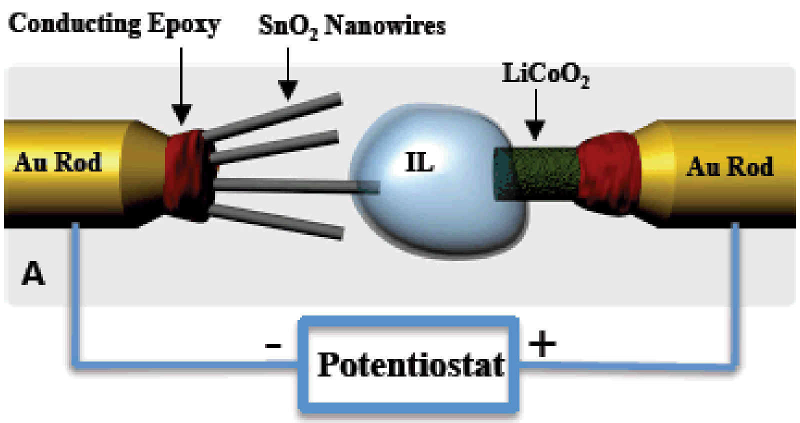
The evolution and function of these surface coatings of Al_2O_3 during cycling are not understood.

Model system: Al nanowire with naturally oxidized surface Al_2O_3 layer



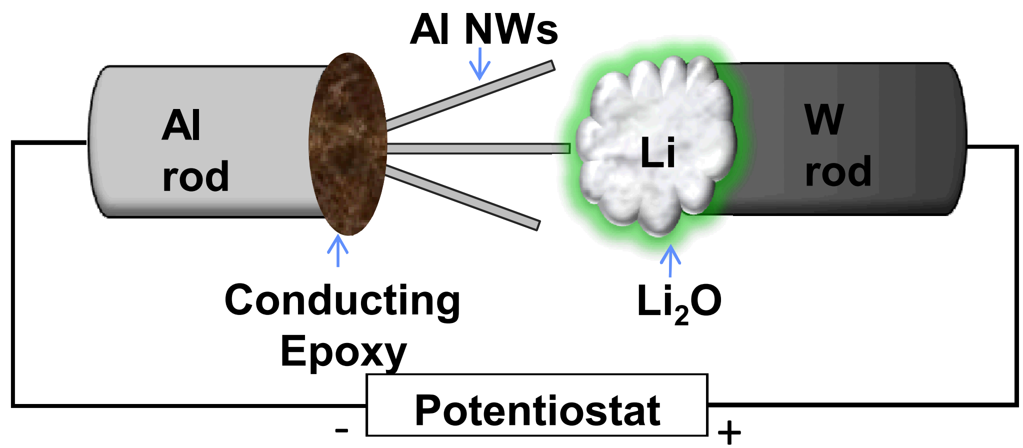
- What causes the pulverization of Al and what's the process like?
- What is the role of the surface Al_2O_3 layer during cycling?

Experimental setup of *in situ* TEM battery test



Huang et al., ***Science*** 330, 1515 (2010)

Introduce a vacuum-compatible electrolyte.

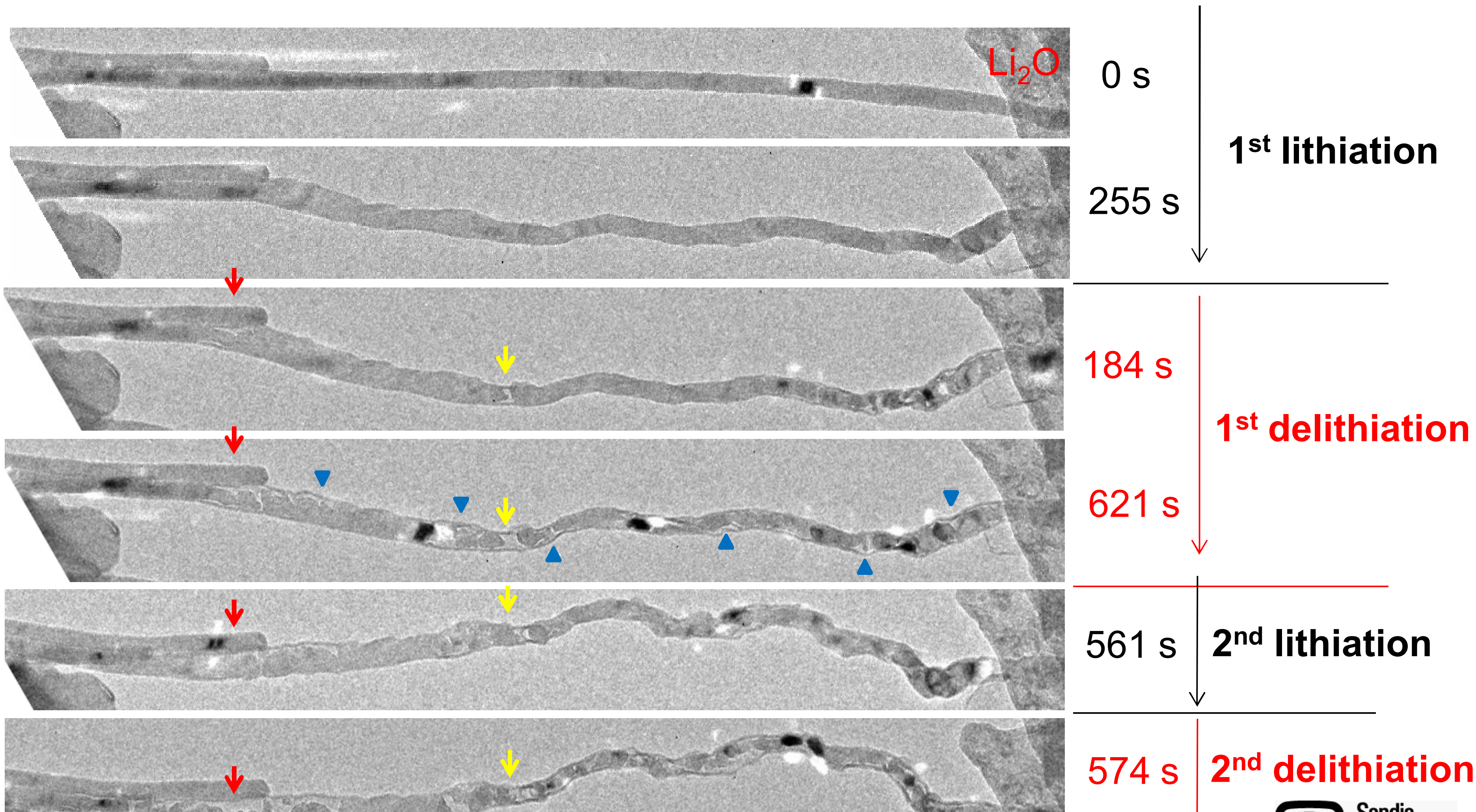


Liu et al., ***Energy Environ. Sci.*** 4, 3844 (2011)

Using the naturally oxidized Li_2O layer on Li metal as the solid electrolyte.

Building a nano-battery in a transmission electron microscope (TEM).
Higher resolution than optical microscopy and real-time observation.

Pulverization of Aluminum Nanowires (1)



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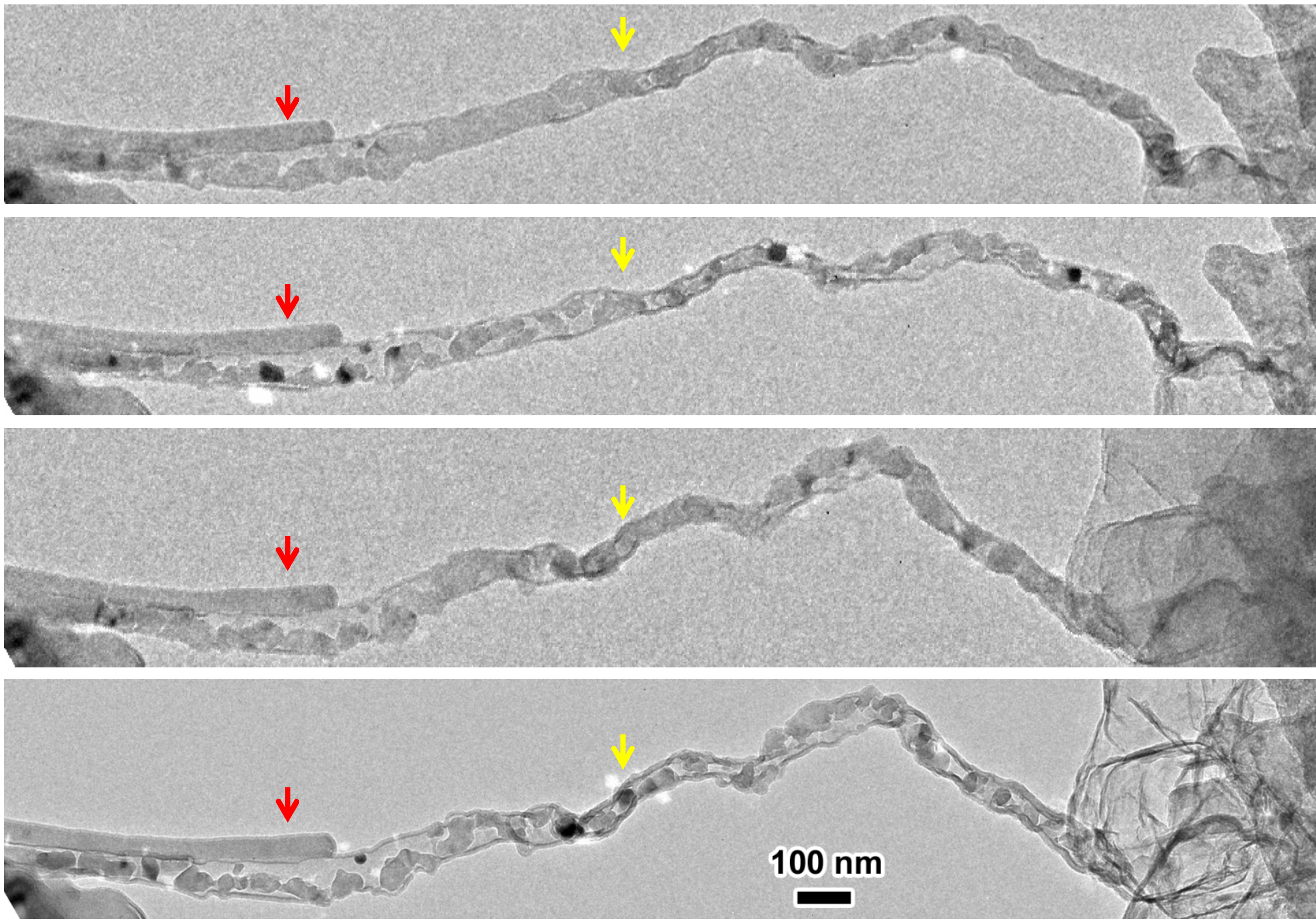
Pulverization of Aluminum Nanowires (2)



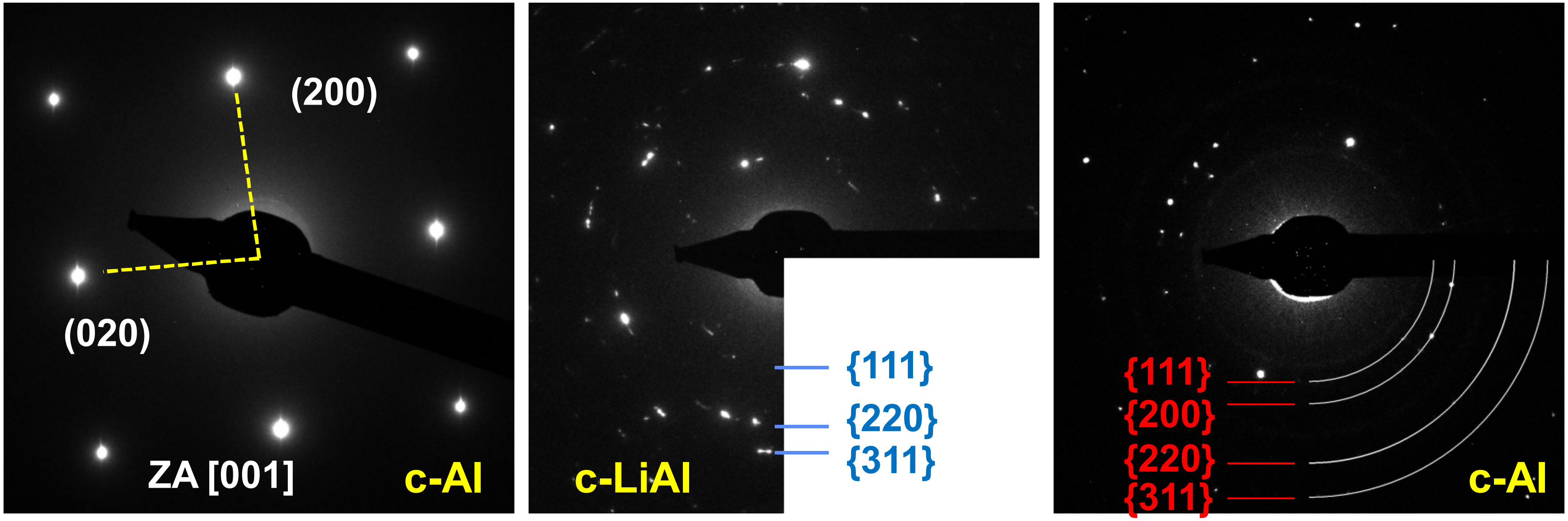
719 s — 3rd lithiation

611 s — 3rd delithiation

1262 s — 4th lithiation

1356 s — 4th delithiation

Lithiated phase of Aluminum Nanowires



Pristine Al NW | Lithiated Al NW | Delithiated Al NW

Electrochemically driven solid state amorphization (ESA) did not occur in the LiAl system.

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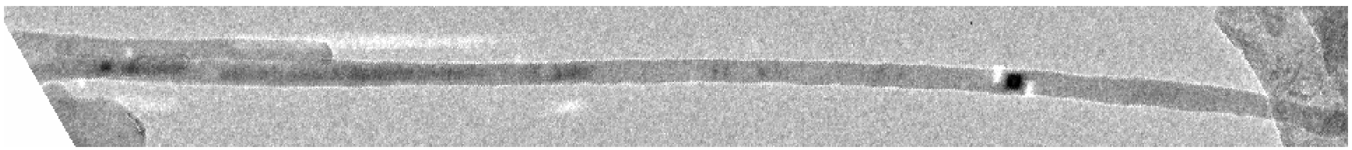
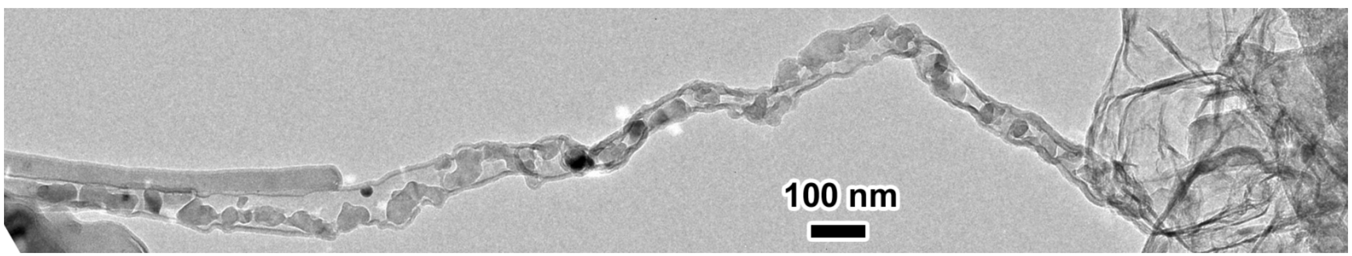
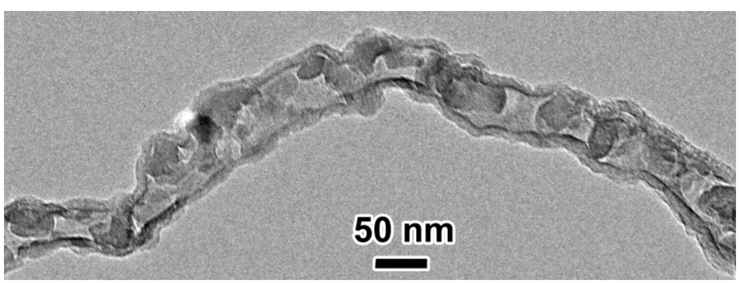
What is the surface tube?

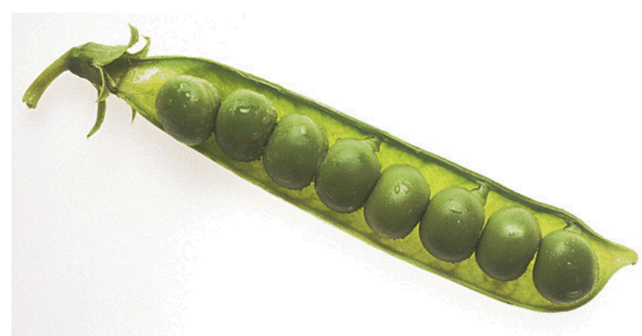


Pristine



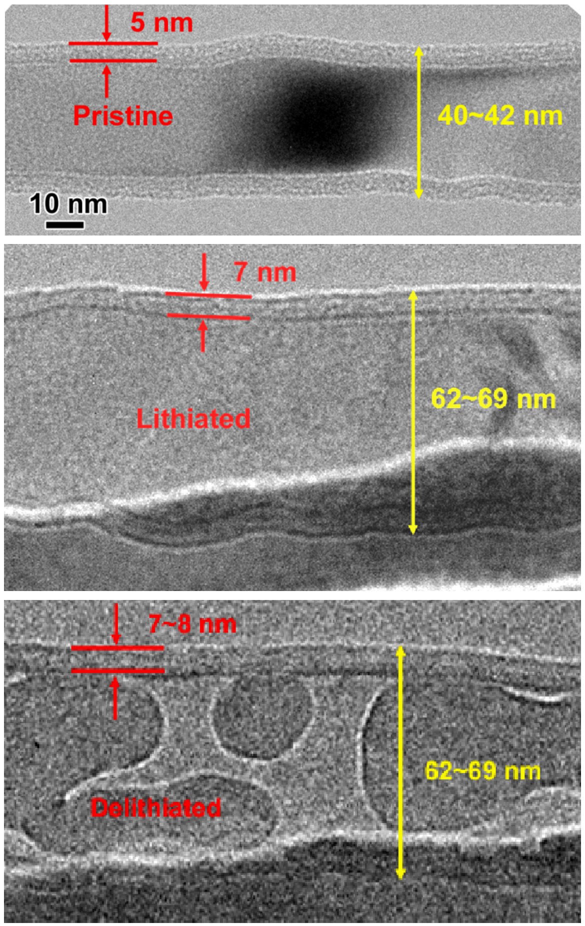
After four cycles

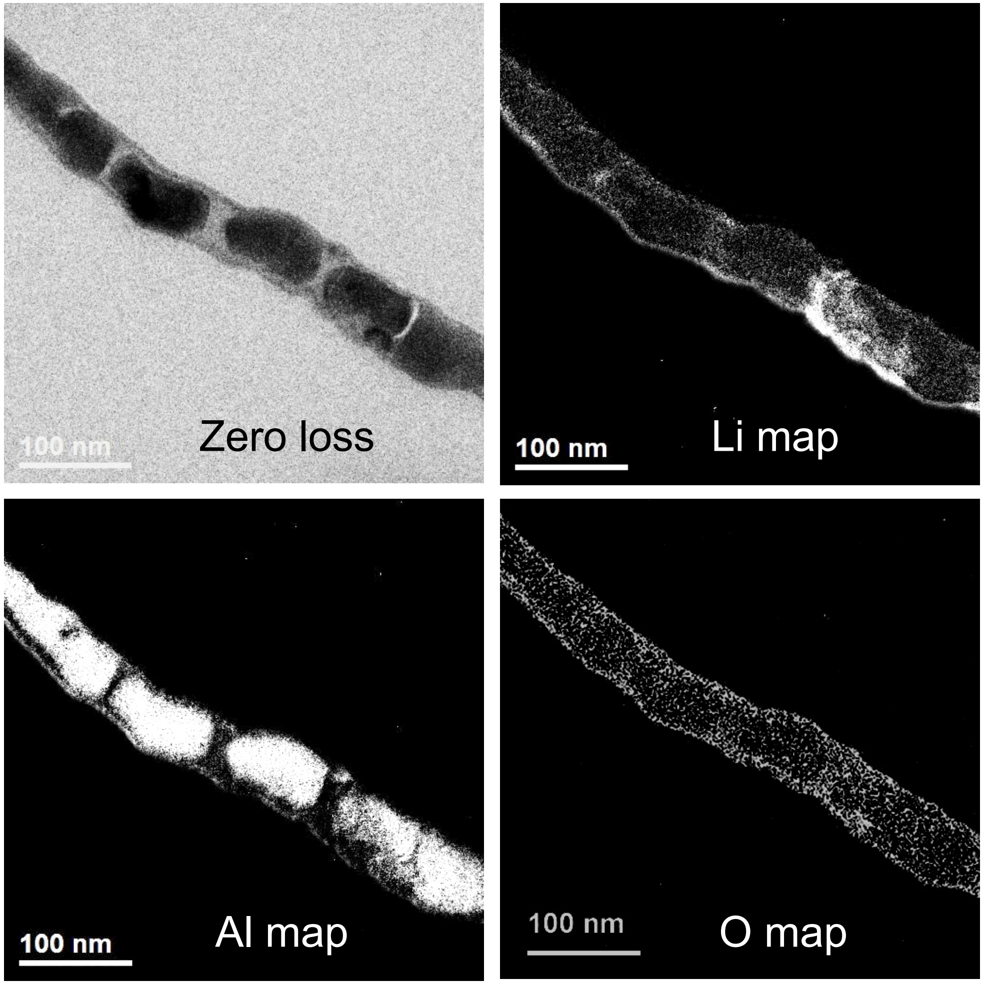




Pea pod from *wpclipart.com*

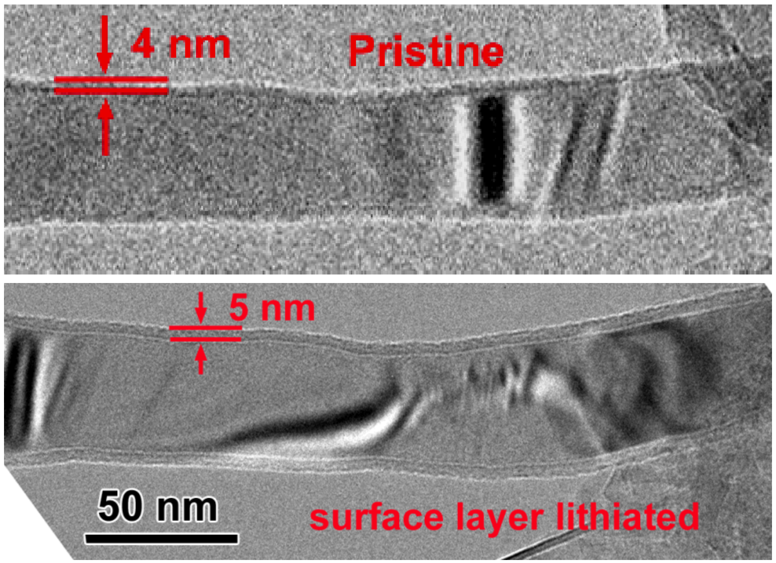
Evolution of the Thin Surface Al_2O_3 Layers (1)

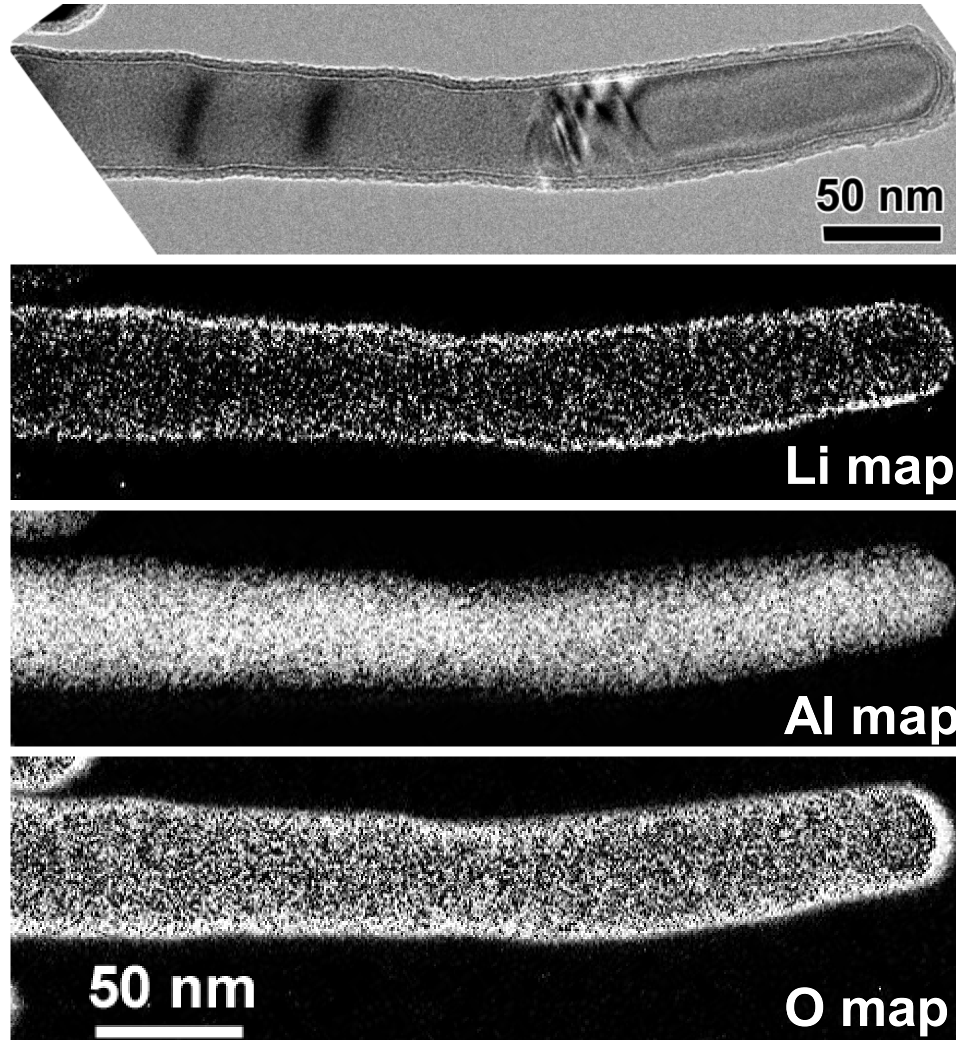




Al_2O_3 Layer was changed into Li-Al-O glass, wrapping the pulverized Al nanoparticles.

Evolution of the Thin Surface Al_2O_3 Layers (2)

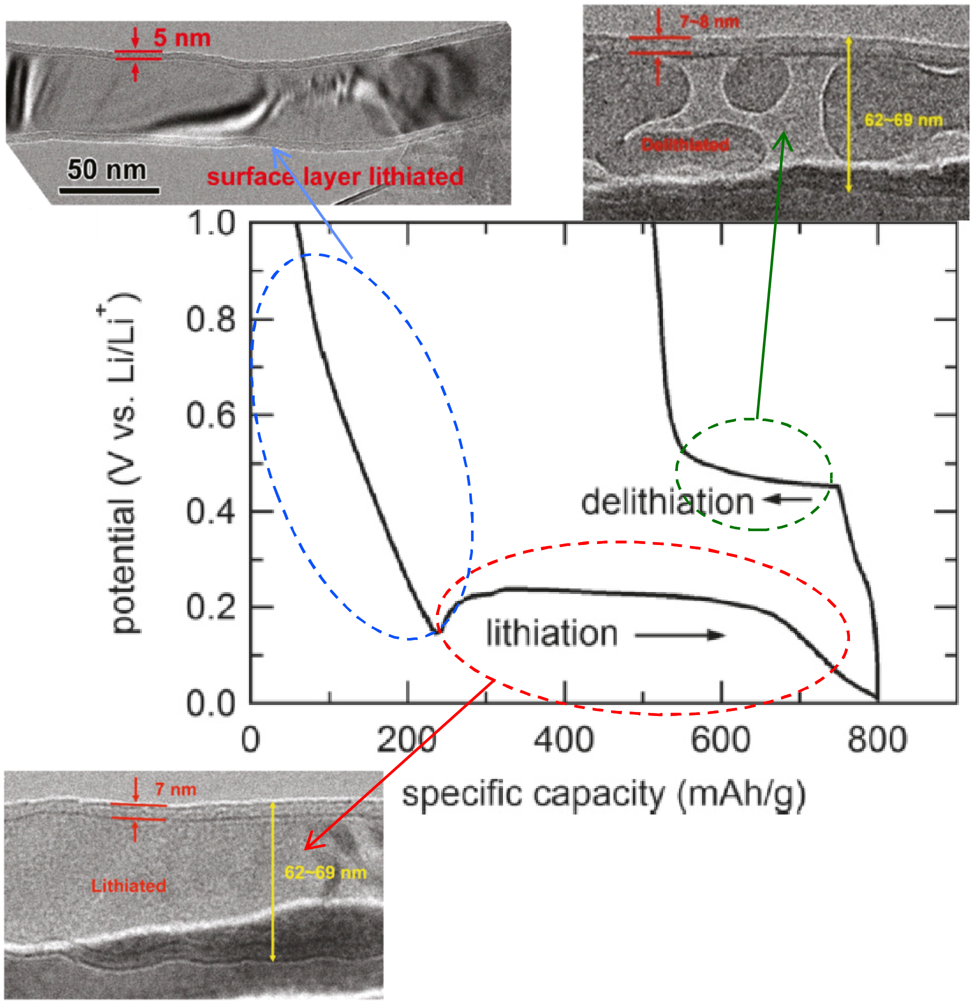


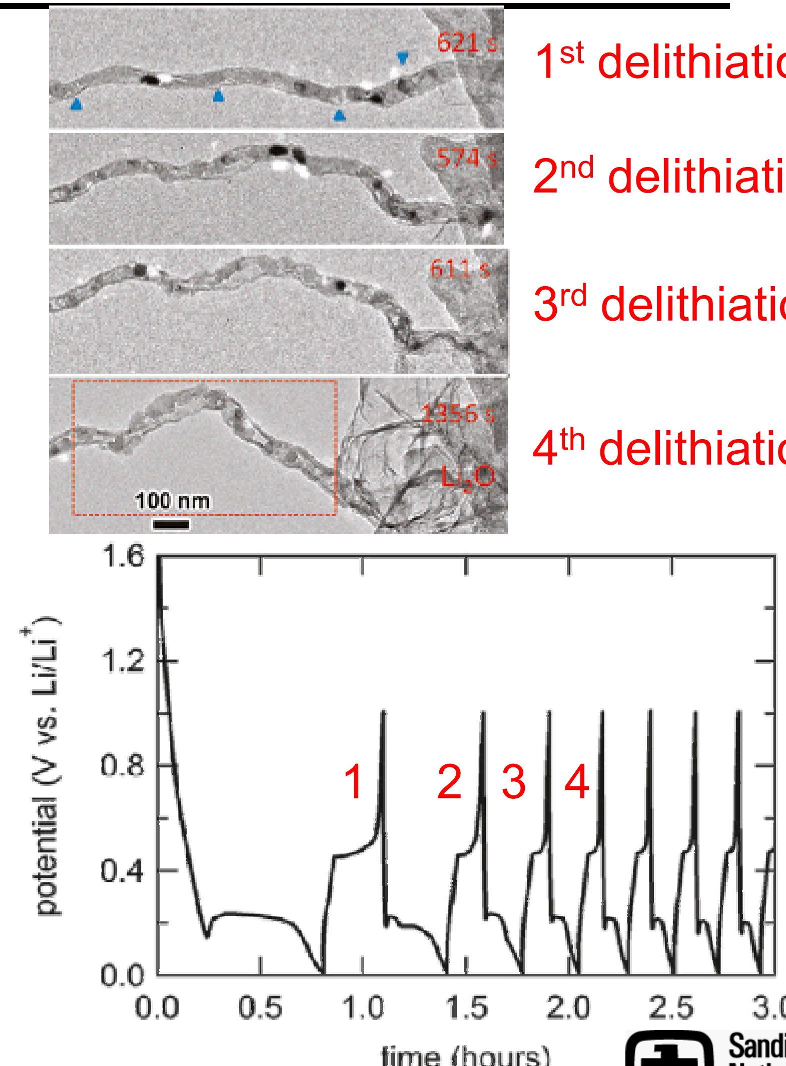


Controlled lithiation of the surface Al_2O_3 Layer

Al_2O_3 Layer was changed into Li-Al-O glass.

Good agreement between *in situ* and *ex situ* (bulk) electrochemistry





1st delithiation

2nd delithiation

3rd delithiation

4th delithiation

Liu, *et al*., ***Nano Lett.*** 2011, 11, 4188-4194

Function of the Thin Surface Al_2O_3 Layers

- The improvement of the performance of LIBs using Al_2O_3 coatings on active materials is attributed to the formation of the Li-Al-O glass layer.
- The Li-Al-O glass layer can provide a facile Li-ion transport path, relative to that in the usually formed solid electrolyte interface (SEI). (like artificial SEI)
- The mechanically robust Li-Al-O glass layer can mitigate mechanical degradation of the active materials to prevent them from breaking off the electrodes.

Conclusions

- The pulverization process of Aluminum NWs upon electrochemical cycling was observed.
- Electrochemically driven solid state amorphization (ESA) did not occur in the LiAl system.
- The surface Al_2O_3 layer was evolved to Li-Al-O glass, which not only acted as a solid electrolyte but also mechanically confined the pulverized nanoparticles to prevent them from losing contact with the current collector.
- Good agreement was found between the in-situ TEM cycling and the conventional electrochemical test cell.

ACKNOWLEDGMENTS

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Thank you very much for your attention!

Literatures about the Li ion conductivity of Li-Al-O glass

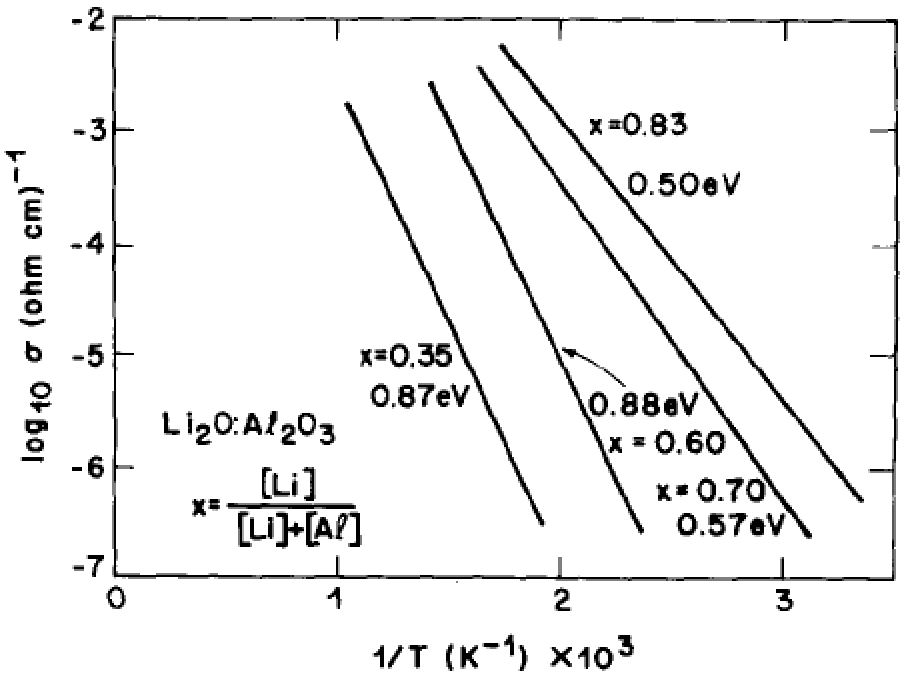

FIG. 1. The ionic conductivity σ of $Li_2O : Al_2O_3$ glasses as a function of reciprocal temperature $1/T$ for various composition ratios.

Up to the order of 1E-6 S/cm at room temperature.

Glass et al. ***J. Appl. Phys.*** 51, 3756 (1980)

About the mechanical properties of Li-Al-O glass

Table 1. Strain on the ALD alumina surface coating and corresponding deformation for different active materials.

Material	Volume expansion	Experimental capacity [m Ahg^{-1}]	Calculated strain	Deformation region
Graphite flakes	10 %[32]	372	3.19 %	Elastic/Plastic
$LiCoO_2$	1.5 %[33]	170	0.45 %	Elastic
Silicon	400 %[10]	~3200	70.9 %	Fracture
Metal oxides	**100–250 %**	**800–1300**	**26–52 %**	**Fracture**

Riley et al., ***ChemPhysChem*** 11, 2124 (2010)

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